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Hydrogen production from catalytic steam reforming of biodiesel byproduct glycerol: Issues and challenges

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ABSTRACT

The objective of this review is to analyze potential technologies and their baseline performance of producing hydrogen from catalytic steam reforming of biodiesel byproduct glycerol. High oxygen content and high impurity level of biodiesel byproduct glycerol, as well as the complex intermediates and high coking potential in its thermal degradation, make the modeling, design, and operation of glycerol steam reforming a challenge. Thermal decomposition characterization of biodiesel byproduct glycerol was covered, and the recent developments and methods for high-purity hydrogen production from glycerol steam reforming were illustrated. The thermodynamics constraint of water gas shift reaction can be overcome by the sorption-enhanced steam reforming process, which integrated catalytic steam reforming, water gas shift reaction and in-situ CO_2 removal at high temperatures in a single stage reactor. The effectiveness of both the enhanced H_2 production and the use of CO_2 sorbents have been demonstrated and discussed. The technical challenges to achieve a stable high-purity hydrogen production by the sorption-enhanced steam reforming process included extending operation time, selecting suitable sorbents, finding a way for continuous reaction-regeneration of catalyst and sorbent mixture and improving process efficiencies. The continuous sorption-enhanced steam reforming of glycerol was designed by a simultaneous flow concept of catalyst and sorbent for continuous reaction-regeneration using two slow moving-bed reactors for high-purity hydrogen production and CO_2 capture, and in this process, catalyst and sorbent were run in nearly fresh state for H_2 production. The sorption-enhanced chemical-looping reforming was also demonstrated. The paper discusses some issues and challenges, along with the possible solutions in order to help in efficient production of hydrogen from catalytic steam reforming of biodiesel byproduct glycerol.

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1. Introduction

Due to the environmental concerns, the global demand for hydrogen is expected to increase greatly in the future for the energy and environmental sustainability [1]. Steam reforming, partial oxidation, auto-thermal reforming, and CO_2 reforming have been widely investigated as primary processes for converting hydrocarbons into hydrogen. Steam reforming is still the most dominant route to convert natural gas as a fossil fuel into hydrogen. Currently, over 50% of the world's hydrogen supply is from steam reforming of hydrocarbons [2]. It is now widely acknowledged that CO_2 in the atmosphere as the greenhouse effect is gradually warming the planet [3]. Carbon capture and storage (CCS) is an important part of the strategy for mitigating the risks of climate change, and CO_2 release from H_2 generation from steam reforming should be recognized. Global efforts in reducing greenhouse gas emissions have spurred intense research in sustainable production methods of hydrogen and CO_2 capture [1,4,5]. Conventional H_2 production from steam methane reforming includes in series of a main catalytic reactor operated at 800–1000 °C, one or two water gas shift reactors operated at 300–450 °C, and at the same time, the products stream is fed to a pressure swing adsorption (PSA) unit where all the gases except H_2 get adsorbed in the beds leading to a high purity H_2 product [6]. The drawbacks of this process are the fossil fuel consumption, CO_2 emission, and the high capital costs due to the separation of CO_2 and H_2.

Biodiesel as the biodegradable, non-toxic, near CO_2-neutral and environmentally beneficial fuel has become more attractive recently as alternative diesel fuel to reduce dependency on fossil fuel imports. The transesterification of renewable biological sources such as vegetable oils and animal fat oils with an alcohol using alkaline or acid catalysts is the most common process for biodiesel production. About 10 wt% of glycerol is produced during the production of biodiesel fuel through the catalytic transesterification process [7]. A increase of biodiesel production all over the world from 2000 year has led to great increment of crude glycerol [8]. Catalytic steam reforming of biodiesel by-product glycerol is a new method to renewable energy conversion. The feasibility for hydrogen production by glycerol steam reforming was carried out by different authors [9–20]. The CFD simulation of glycerol steam reforming indicated the parameters including temperature, ratio of steam to carbon (S/C), residence time, inlet gas composition and flow rate should be carefully controlled to maximize H_2 production with minimum coke formation [12,13]. One of the difficulties for the utilization of hydrogen from glycerol steam reforming by catalysts is high CO_2, CO and CH_4 contents. In addition, the demand for high-purity hydrogen production is rapidly growing in the electronics, fine ceramics, and fine chemical industries. Hence, we need a better system to high-purity hydrogen production from renewable resources to decrease fossil energy and control the CO_2, and it is preferred the steam reforming, water gas shift reaction (WGS) and CO_2 removal can be conducted in one single step at a low temperature and pressure. A technology as the sorption-enhanced steam reforming has been proposed and investigated for hydrogen production with simultaneous CO_2 abatement [21–26]. It is based on the concept of combined reaction and separation, which uses a catalyst phase and an adsorbent phase in a reactor. The technology offers a number of advantages including high conversion of hydrocarbons feed, low operating temperature of reforming reactor and enhanced heat transfer of process. In addition, the capital cost can be reduced as the number of processing steps required for subsequently separating CO_2 is decreased. The renewable hydrogen from biomass-derived resources is a major challenge as global energy generation and fuel cell application. This paper gives an overview of the research progress in catalytic steam reforming of glycerol, and highlights the issues and challenges for high-purity hydrogen production by the sorption-enhanced steam reforming process.

2. Thermal decomposition characterization of biodiesel byproduct glycerol

The thermal decomposition of the fuel was found to play a significant role in the H_2 production and coke formation during catalytic steam reforming process [27]. A typical sample of crude glycerol from biodiesel production mainly consisted of 70–90 wt% glycerol and the average elemental molar formula was $C_{3\pm0.2}H_{8.9\pm0.4}O_{3.4\pm0.2}N_{(5\pm2)\times10^{-3}}$ [28]. The results of GC–MS analysis showed the sample of crude glycerol includes glycerol and methyl esters products of the biodiesel process such as linoleic ($C_{19}H_{34}O_2$), palmitic ($C_{17}H_{34}O_2$), oleic ($C_{19}H_{36}O_2$), and stearic ($C_{19}H_{38}O_2$) acid methyl esters. Biodiesel byproduct glycerol often contains many impurities and is a very poor fuel used in either petrol or diesel engines [9]. It can be purified and used in the food industry, pharmaceuticals or water treatment for digestion. The work by Yang et al. has successfully converted the crude glycerol by fermentation to obtained up to 1,3-propanediol [29]. However, these processes are very expensive and exhibit a low yield [9]. Glycerol as a potential feedstock via pyrolysis, or gasification to produce H_2, CO or other fuel gases has received considerable research attention [28,30–33]. Valliyappan et al. reported the hydrogen or syngas production from glycerol pyrolysis at high temperatures and the gas products were CO, H_2, CO_2, CH_4 and C_2H_4 [30]. The glycerol pyrolysis was studied in a laminar flow reactor by Stein et al., and the results showed that the initial decomposition products were H_2O, CO, CH_4, CO_2, acetaldehyde and acrolein, and then acetaldehyde and acrolein further were decomposed to produce primarily CO and H_2 [31]. Buhler et al. carried out the thermal decomposition of glycerol in near-critical and supercritical water and they reported the main products include methanol, acetaldehyde, ethanol, CO, CO_2 and H_2 [32]. In fact, it is also very difficult to understand the thermo-chemical characteristics of the crude glycerol from the biodiesel production process. Dou et al. studied the pyrolysis of crude glycerol from a biodiesel biorefinery in dry N_2 was by thermogravimetry coupled with fourier transform infrared spectroscopy (TGA–FTIR) [28]. The difference in the mass loss obtained by TGA may be due to the degradation of the different components at different temperatures. The FTIR indicated that the concurrent and dehydration reactions of gas-phase pyrolysis of crude glycerol at low temperatures may lead to the formation of the products such as liquid, gas and coke, and at high temperatures, consecutive thermal cracking reactions were predominant to form H_2, CO, CO_2, CH_4 and carbon [28]. Some species such as H_2CO, HCO and CH_2OO may undergo the decomposition to product CO, CO_2, H_2O and H_2 at high temperatures [34]:

$$H_2CO \rightarrow H_2 + CO \quad (R1)$$

$$H_2COO \rightarrow H_2O + CO \quad (R2)$$

$$H_2COO \rightarrow H_2 + CO_2 \quad (R3)$$

The major drawback of glycerol pyrolysis is carbon formation due to the cracking of some hydrocarbons including CH_4 [30]:

$$C_xH_y \rightarrow \frac{y}{2}H_2 + xC_s \quad (R4)$$

The thermogravimetic experimental data were interpreted by an improved iterative Coats–Redfern method [28]. For the pyrolysis of crude glycerol, a number of forms of the mechanism function were also tested with the experimental data, including: the power law model, the reaction order model, 1–3D diffusion

models. The results of the kinetic analysis indicated that the first order power law model predicted accurately the main (second) and third phases in the pyrolysis of the crude glycerol and the 3-D diffusion model more accurately reproduced the 4th phase. It can be observed that the values of kinetic parameters such as E and A can be different for four heating rates, indicating the thermal decomposition of crude glycerol may depend on the experimental conditions. As the heating rate is increased, the maximum mass loss and/or maximum rate of decomposition shift to higher temperatures. This can be attributed to the variations in the rate of heat transfer with the change in the heating rate and the short exposure time to a particular temperature at high heating rates, as well as the effect of the kinetics of decomposition [28].

3. Catalytic steam reforming of glycerol for H_2 production

3.1. Thermodynamic calculation of glycerol steam reforming

The thermodynamic analysis calculated by the method of minimization of Gibbs free energy will also be informative for producing hydrogen from glycerol, which provides a comprehensive understanding on the optimal condition, product distribution and energy efficiency. A thermodynamic analysis of oxidative steam reforming of glycerol for hydrogen production was carried out with Aspen plus TM by Yang et al., and the results showed that higher C/O (carbon-to-oxide ratio) and S/C (steam-to-carbon ratio) ratios favor the production of hydrogen from glycerol [35]. The effects of the process variables on hydrogen production from glycerol by the direct minimization of Gibbs free energy were analyzed and the optimal condition was discussed thermodynamically to inhibit carbon deposition by some studies [36,37]. The thermodynamics analysis of dry reforming glycerol and autothermal reforming of glycerol to produce hydrogen or syngas were carried out by Wang et al. [38,39], and they concluded that the temperatures above 750 °C and S/G (steam-to-glycerol ratio) between 2:1 and 3:1 at 20–50 atm are suitable for synthesis gas production [38,39]. More carbon can be produced during glycerol dry reforming compared with steam reforming.

Table 1
Main equations on thermodynamic analysis of glycerol steam reforming [2,11,14,44,45].

Glycerol steam reforming	
$dG = \sum_{i=1}^{N} \mu_i dn_i = 0$	(1)
$\sum_{i=1}^{N} a_{ji} n_i = b_j, \quad j = 1, \ldots, M$	(2)
$G' = \sum_{i=1}^{N} \mu_i n_i + \sum_{j=1}^{M} \lambda_j \left(\sum_{i=1}^{N} a_{ji} n_i - b_j \right)$	(3)
$\Delta G_i^f / RT + \ln(n_i/n_T) + \ln P + \ln \hat{\phi}_i + \sum_{j=1}^{M} \lambda_j a_{ji}/RT = 0, \quad i = 1, \ldots, N$	(4)
$n_T = \sum_{i=1}^{N} n_i, i = 1, \ldots, N$	(5)
With CO_2 removal	
$\Delta G_{CO_2}^f / RT + \ln(n_{CO_2}/n_T) + \ln P + \ln \hat{\phi}_i + \lambda_C + 2\lambda_O)/RT = 0$	(6)
$\Delta G_{CO_2}^f / RT + \ln(n_{CO_2}(1-f)/n_T) + \ln P + \ln \hat{\phi}_i + (\lambda_C + 2\lambda_O)/RT = 0$	(7)
$n_T = \sum_{i=1}^{N} n_i - n_{CO_2} f, \quad i = 1, \ldots, N$	(8)
Nitrogen used	
$2n_{N_2} = 2(1 + WGFR)/FI$	(9)
$\Delta G_{N_2}^f / RT + \ln(n_{N_2}/n_T) + \ln P + \ln \hat{\phi}_i + (2\lambda_N)/RT = 0$	(10)

n_i is the molar concentration of component i in the system and μ_i is the chemical potential of component i, a_{ji} is the number of j type atoms in the i species and b_j refers to number of j type atoms in the feed, λ_j is the Lagrangian multipliers, R is the universal gas constant, n_T is the total molar number of species, $\hat{\phi}$ is the fugacity coefficient in the gas mixture, ΔG_i^f is the standard Gibbs free energy of formation, f is the fraction of CO_2 removed, FI refers to the molar ratio of the mixture of steam and glycerol to nitrogen.

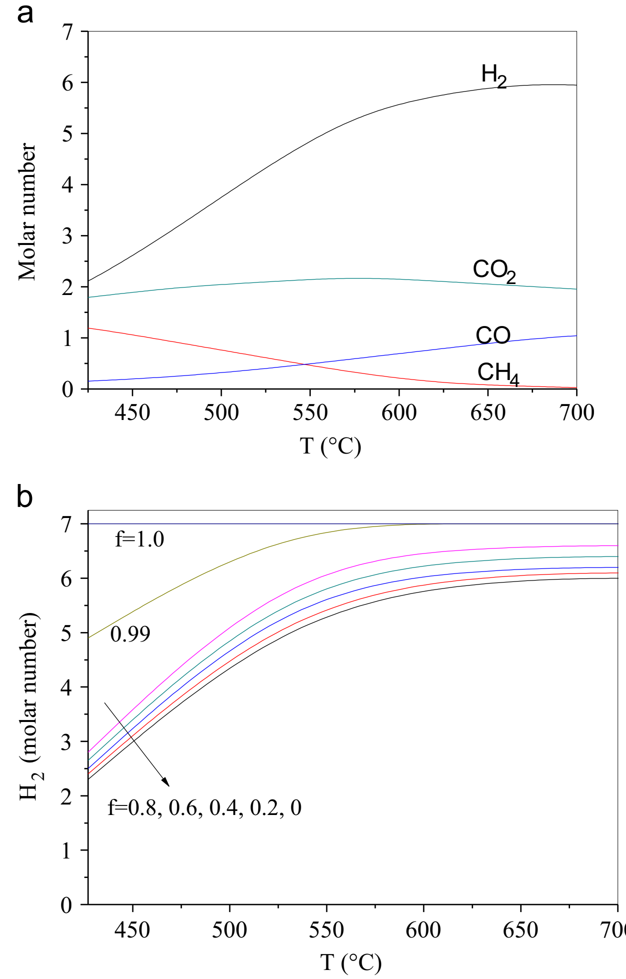


Fig. 1. Effect of temperature on hydrogen production by glycerol steam reforming (a) without and (b) with in-situ CO_2 removal.

The thermodynamic analysis on the effects of CO_2 removal to glycerol steam reforming has also been reported by some studies [2,11,40–44]. Alvarado and Gracia carried out a thermodynamic analysis of the use of hydrotalcites as CO_2 adsorbent in glycerol reforming, and the results showed H_2 yield is maximized between 350–450 °C and S/G ratio above the stoichiometric ratio [41]. A detailed comparative study on thermodynamic and experimental analyses of glycerol steam reforming for hydrogen production with or without CO_2 removal has been conducted in terms of the effects of temperature, pressure, S/G, feeding reactants to inert gas ratio and feeding gas flow rate and the thermodynamic and experimental data agree fairly well [44]. Chen et al. investigated the effect of adding sorbent of CO_2 on the glycerol steam reforming using thermodynamic method [11,45]. The main equations solved by using an in-house Fortran Code based on the DNEQNF subroutine of the IMSL library for thermodynamic analysis on the effects of removing CO_2 to glycerol steam reforming are summarized in Table 1 [2,11,14,44,45]. Effect of temperature on equilibrium constant was calculated and Fig. 1 shows the compositions in glycerol steam reforming without and with in-situ CO_2 removal under the conditions of S/C=3:1 and the temperature of 425–700 °C [2,11,14,45]. The upper limit of the molar number of H_2 for glycerol steam reforming is 6.0, and the molar numbers of H_2 and CO increase with increasing temperatures [44]. CO_2 removal enhances H_2 production and reduces CH_4 and CO production. In the ideal scenario of 100% CO_2 removal, 7.0 mol of H_2 and zero moles of CH_4 and CO are yielded [2].

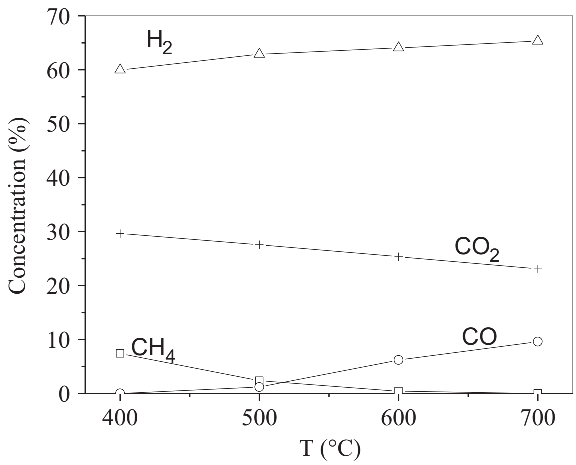


Fig. 2. Concentrations of average product gases at different temperatures for glycerol steam reforming.

3.2. Glycerol steam reforming

The glycerol steam reforming by different catalysts to produce hydrogen may be considered to occur first through glycerol dehydrogenation to leave CO bonded onto the catalyst surface, which could then undergo desorption, followed by water gas shift or methanation reaction. Hirai et al. reported that glycerol steam reforming over a Ru/Y_2O_3 catalyst exhibited a H_2 selectivity of 90% and a glycerol conversion of 100% at 600 °C [46]. Araque et al. studied that hydrogen production by glycerol steam reforming over CeZrCo fluorite type oxides using two CZCo and CZCoRh mixed oxides [4,47]. For the CZCoRh diluted with SiC, the conversion to gaseous products is very high and the production of H_2 remains constant and High CO concentration may be attributed to reverse water shrift reaction at high temperatures. Adhikari et al. studied glycerol steam reforming using Ni/CeO_2, Ni/MgO, and Ni/TiO_2 catalysts and the Ni/CeO_2 was found to be the best catalyst for H_2 selectivity of 74.7% and a glycerol conversion of 99% obtained at 600 °C [16]. The glycerol steam reforming process was evaluated using an alumina-supported metal catalyst and the results showed that high H_2 production was reached at high temperatures and selectivity of up to 70% was obtained [48]. Czernik, et al. studied H_2 production from catalytic steam reforming of biomass-derived liquids by a commercial nickel based naphtha reforming catalyst [49], and such a catalyst was chosen also because of its high activity and low cost. NiO/Al_2O_3 catalyst typically used for steam methane reforming was investigated to produce H_2 for steam reforming of glycerol using a range of the steam-to-carbon ratio from 1.1 to 4.0 at temperatures between 450 °C and 550 °C [50]. The results showed that H_2, CO_2 and CO were the main gaseous products with H_2:CO_2 ratio at approximately 2.15 while H_2:CO ratio varied between 6.0 and 16.0 depending on the reactant feed composition [50]. Some studies showed that NiO/Al_2O_3 presented the performance reaching above 65% of H_2 yield, and Ce, Mg, Zr, and La modifying NiO/Al_2O_3 could enhance hydrogen selectivity [16,51]. Monometallic and bimetallic catalysts of Ni and Pt on Al_2O_3 were modified with La_2O_3 to improve their behaviors; the best H_2 selectivity was obtained with 6 wt% La_2O_3 on NiO/Al_2O_3 [51]. Ni and Ni–Pt catalysts produced a significant formation of CH_4, while Pt catalysts showed high production of oxygenated hydrocarbons [52]. Glycerol steam reforming was studied on Ni/CeO_2, Ni/Al_2O_3, and Ni/CeO_2-promoted Al_2O_3 catalysts, and the incorporation of low ceria loadings enhanced their catalytic activity, while high ceria contents decrease the catalyst capacity to convert intermediate oxygenated hydrocarbons into H_2 [53]. Ni/Al_2O_3 catalyst suffer deactivation during the steam reforming of oxygenated hydrocarbons due to coke deposition [54], the study also showed that using Ni/Al_2O_3 modified with ZrO_2 and CeO_2, Ni–Ce catalyst displayed a great stability [55]. It may be due to the Ce effect in inhibition of secondary dehydration reactions forming unsaturated hydrocarbons, which are coke precursors generating fast catalyst deactivation [4,56]. The studies also showed that Ni/Al_2O_3 catalyst with the moderate Ni reduction degree, high Ni dispersion, and small nickel particle size could possess the highest H_2 yield from glycerol steam reforming [57]. Pompeo et al. studied H_2 production by glycerol steam reforming with Pt/SiO_2 and Ni/SiO_2 catalysts, and the results would indicate that Ni and NiPt catalysts have the same reaction pathways [58]. They argued that the neutral SiO_2 properties do not favor the glycerol dehydration. Besides, due to the low CH_4 content in gaseous products, it is reasonable to think that the C–C cleavage predominates over the C–O cleavage [18,58]. Bobadilla et al. studied the effects of the shape of Ni catalysts on the glycerol steam reforming; the results showed the morphology of catalyst is responsible for different behavior during reforming reaction and catalyst with high resistance to coke formation was also prepared [59]. Ni catalysts supported on La_2O_3–SiO_2 were tested by Thyssen et al. and the results showed the deposition of carbon on the catalyst greatly affects steadily as the increased proportion of La_2O_3 in the support [60]. Araque studied that effect of the active metals on H_2 production from glycerol steam reforming using CeZr (Co,CoRh) catalysts and thermal decomposition of glycerol is superimposed with its steam reforming [4]. It is also difficult to make a distinction between decomposition and steam reforming, however, all the coke formation should be attributed to thermal decomposition of glycerol and its intermediates.

Catalysts studies in glycerol steam reforming have been reviewed by Lin [61]. Most of the studies were mainly focused on noble metal-based catalysts for hydrogen production from glycerol and commercially available catalysts with low cost have still great demand. To make use of glycerol to increase its values and low-cost catalysts, we carried out H_2 production from catalytic steam reforming of glycerol by Ni–Mg–Al, Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg, Ni–Al catalysts in a fixed-bed reactor under atmospheric pressure within a temperature range of 450–650 °C [14,15]. All the catalysts show larger particles in a state of aggregation and also have an irregular morphology. Al_2O_3 can be observed as large particles and all of the NiO is observed to remind the octahedral morphology. High CuO loading in the prepared Ni–Cu–Al catalyst is the likely significant agglomeration of crystallites. The filamentous carbons deposition phenomenon was observed in the reacted catalysts that some of the catalyst particles were cracked and fragmented into small particles after steam reforming process, and a surface breakup by carbon was obvious. The typical products of glycerol steam reforming as shown in Fig. 2 indicated that H_2, CO_2, CO and CH_4 are major gaseous products, both production of H_2 and CO_2 are strongly depending on temperature [14]. The conversion of glycerol is also found to be greater than 95% at the temperature of higher than 500 °C and the conversions of steam is about 22–25% [14]. The effects of the operating conditions including temperature, the ratio of steam to carbon (S/C), glycerol inlet concentration and flow rate of carrier gas on glycerol steam reforming by Ni–Mg–Al based catalyst were tested [14]. The studies also showed a progressive deactivation of the catalyst due to the formation of carbon residues was accompanied by a decrease of conversion to gas products [15]. The removal of carbons deposited on the catalyst was measured by TGA experiments during medium temperature oxidation [14,15]. Glycerol steam reforming usually occurs during gaseous phase processing under ambient pressure. This requires substantial heat inputs to vaporize reactants, and demands considerable process heats.

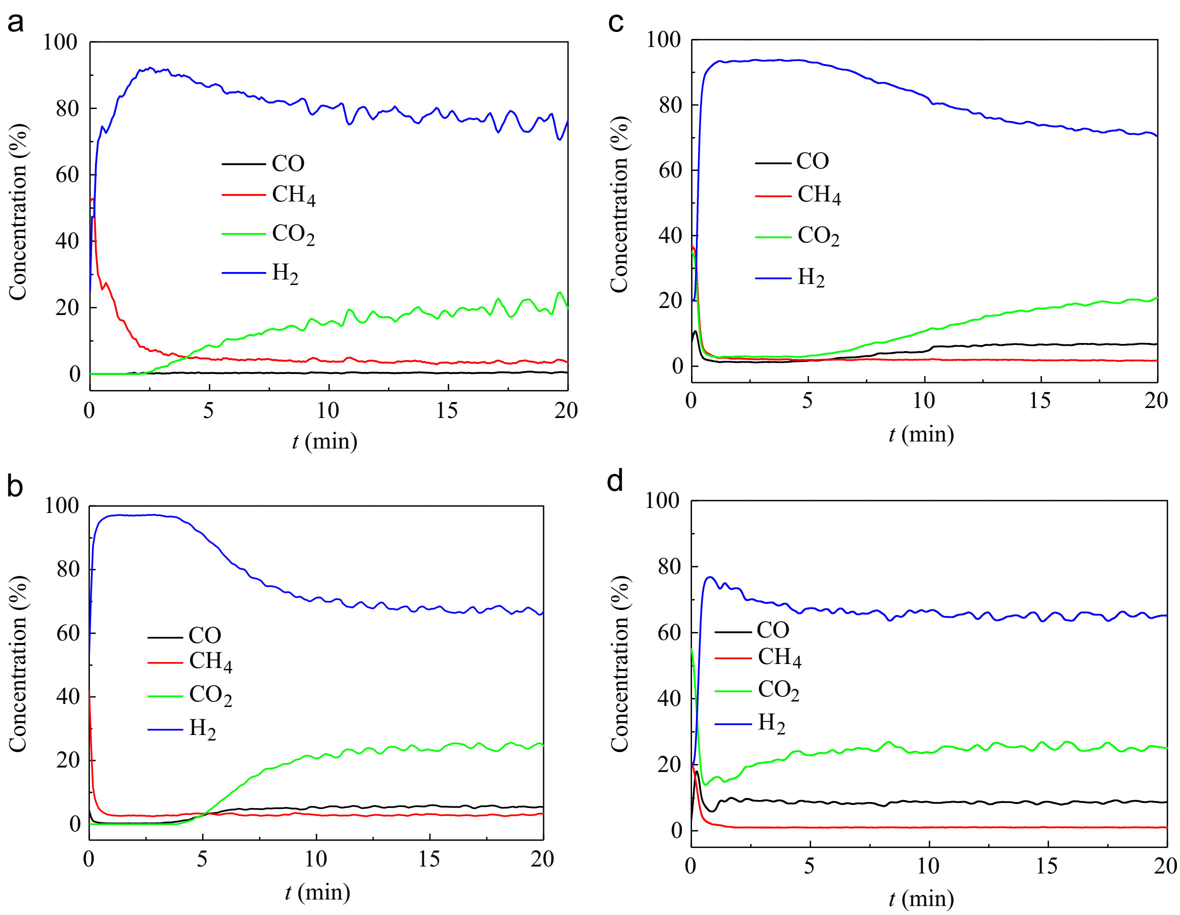


Fig. 3. Gas products vs time for glycerol steam reforming with in-situ CO_2 removal at different temperatures: (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

3.3. *Enhanced hydrogen production with in-situ CO_2 removal*

The technology has been made for enhanced hydrogen from light hydrocarbons, methanol, ethanol or sunflower oil by using steam reforming reaction with in-situ CO_2 removal [27,62–64]. There is merit in studying the sorption-enhanced steam reforming of glycerol. He et al. reported hydrogen production from catalytic steam reforming of crude glycerol with in-situ CO_2 removal in a fixed-bed reactor over a mixture of Ni/Co catalyst derived from hydrotalcite-like material and dolomite as CO_2 sorbent [42]. In their work, the applied operating window was at a steam-to-glycerol ratio in a range of 3–9 and a temperature of 500–650 °C. The obtained hydrogen content or purity was close to the theoretical boundary at temperature of higher than 575 °C and S/G ratio of no less than 4 [42]. Wu et al. studied that sorption of carbon dioxide for enhanced steam reforming to produce hydrogen via Ni–CaO–Al_2O_3 catalysts derived from hydrotalcite-like compounds, and the results showed the materials performed excellent CO_2 adsorbent capacity and reforming activity [65]. The time for the breakthrough on in-situ CO_2 removal during steam reforming depends on both the amount of the sorbent and its capacity. We investigated experimentally the effects of CO_2 removal by sorbent from the dolomite on glycerol steam reforming [66,67]. The typical results are shown in Fig. 3 [2,45,66]. In the case of addition of a CO_2 acceptor to the reactor, CO_2 is converted to a solid carbonate, and thereby could directly produce high-purity H_2. As can be seen, the H_2 purity with in-situ CO_2 removal in the initial reaction period was substantially higher than theoretical limit of glycerol steam reforming using a conventional catalyst-only reactor. The CO_2 concentrations can be kept at around 0 vol% and very small amounts of CO and CH_4 are observed. The operation duration for high-purity hydrogen production is less than 5 min for the temperatures of 400–600 °C under the experimental conditions. The product composition with high-purity hydrogen can remain steady for a rather long time if the reactor is loaded with an excess of catalyst and sorbent, however, the time lasts also very limited, and with an increase in the time-on-stream, there is a gradual deterioration of CO_2 removal as the sorbent begins to saturate. Eventually the process and compositions of the product gases degrade to the conventional steam reforming of glycerol with catalyst-only behavior.

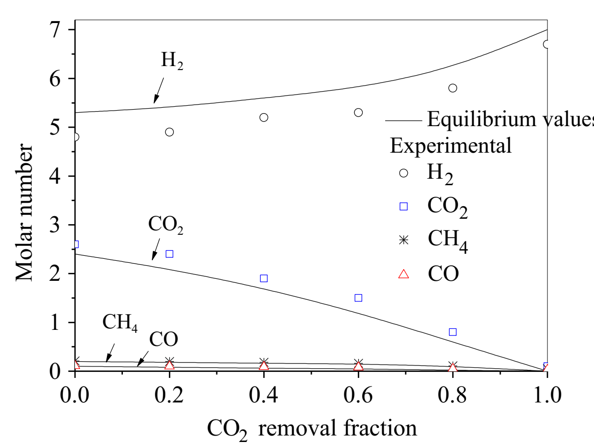


Fig. 4. Equilibrium and experimental effect of CO_2 removal on products in glycerol steam reforming.

In order to clarify the effects of SERP, the initial molar number of glycerol was taken as 1 mol and Fig. 4 shows the compositions in glycerol steam reforming with different in-situ CO_2 removal in

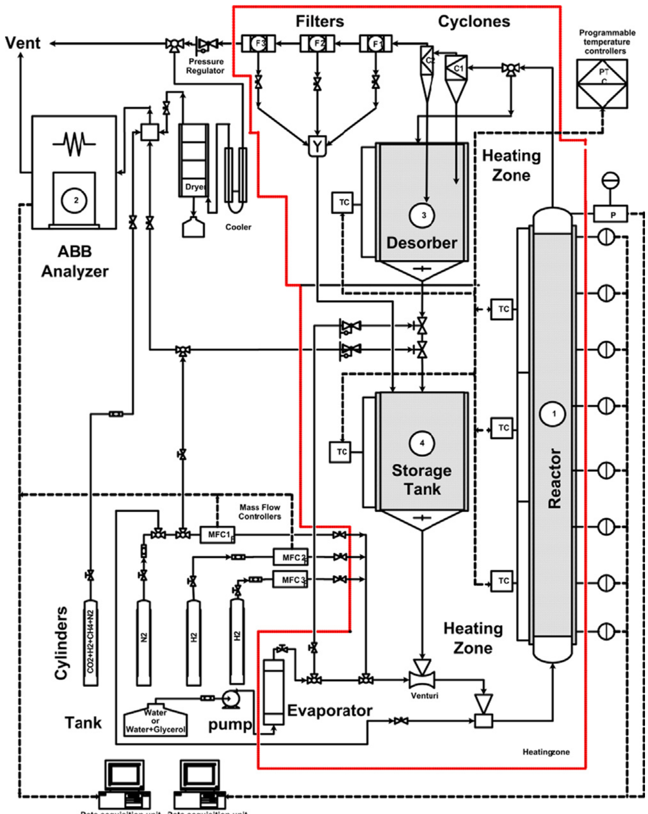


Fig. 5. Experimental system on enhanced hydrogen production with in-situ CO_2 removal using sorbent circulation.

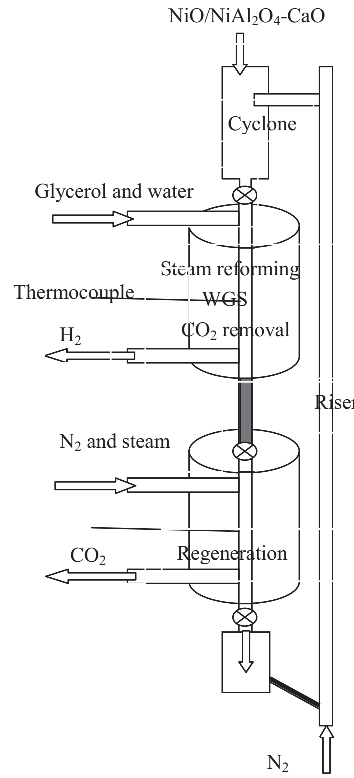


Fig. 6. Schematic drawing of CSERP system by moving-bed reactors.

first cycle. The experimental molar numbers of H_2, CO_2, CH_4 and CO were compared with thermodynamic calculations. As can be seen from Fig. 4, an increase in CO_2 removal enhances H_2 production and reduces CH_4 and CO production. The enhancement of H_2 production is particularly significant when over 80% CO_2 is removed. In the ideal scenario of 100% CO_2 removal, H_2 of 7.0 mol are yielded per unit mole of glycerol. H_2 production is seen to be enhanced greatly with CO_2 in-situ removal. Considering the discrepancy in experimental and equilibrium H_2 production, it could also have been caused by catalyst effects and the absence of solid C in the equilibrium predictions [67]. Enhancement in the production of high-purity H_2 obtained by steam reforming is limited by the thermodynamics of WGS reaction. However, this constraint has been overcome by concurrent WGS and carbonation (of calcium oxide) reaction to enhance H_2 production. The calcium oxide forming calcium carbonate incessantly drives the equilibrium-limited WGS forward by removing the CO_2 product from the reaction mixture, which will ensure a high yield and purity of H_2. The SERP scheme not only improves the H_2 yield and purity but also integrates a CO_2 management scheme and gas cleanup in the hydrogen production process. At the same time, high coking potential of glycerol and fatty acid methyl esters in crude glycerol will also result in the increased formation of coke, thus decreasing H_2 yield and catalyst activity.

4. Challenges in glycerol steam reforming with in-situ CO_2 removal

4.1. How to extend the operation time?

High-purity hydrogen production by the sorption-enhanced steam reforming depends on in-situ CO_2 removal [66–68]. The studies have reported the experimental and calculated H_2 production by sorption-enhanced steam reforming of glycerol for in-situ CO_2 removal [66,67]. However, the problem of the SERP for practical application is to find a way for the regeneration of sorbent and to extend the operation time. Chen et al. studied a system with sorbent particle flow for reaction and regeneration. The experimental system is shown in Fig. 5 [2,45]. It consisted of a packed column, two cyclones in series for particle separation, a particle injection unit for introducing suspended particles into the packed bed, a hopper for collecting particles from the cyclones and for dispensing the particles to the particle injection unit, and various flow measurement and control devices. A commercial nickel-based catalyst and a sorbent of potassium promoted Mg–Al hydrotalcite were used. The sorbent was regenerated by circulating the particles together with a mixture steam and nitrogen N_2 at 500 °C. The results showed that the use of sorbent always leads to a higher H_2 production in comparison to that without the sorbent. However, the extent of enhancement is very small, and particles plugging phenomenon was very serious because it is not easy for sorbent particles to pass the bed pore formed by the catalyst particles. Another technical challenge is coking. Chen et al. further proposed if the inert gas is replaced by steam [2,45], hydrogen production should be enhanced considerably and coke can be reacted with steam, at the same time, this option will not only decrease the partial pressure of glycerol but also, increases the reactant water, and based on the Le Chatelier's principle, both two effects could enhance the forward reaction.

Some studies have demonstrated that a single fluidized bed (FB) reactor in a gas switching mode or a circulating fluidized bed reactor would be particularly useful in the sorption-enhanced steam reforming process due to continuous cyclic regeneration of the sorbent [69–73]. A work of SE-SMR in a circulating fluidized bed reactor with calcined natural dolomite as CO_2 sorbent and Ni/$NiAl_2O_4$ as catalyst was reported, and the system includes two

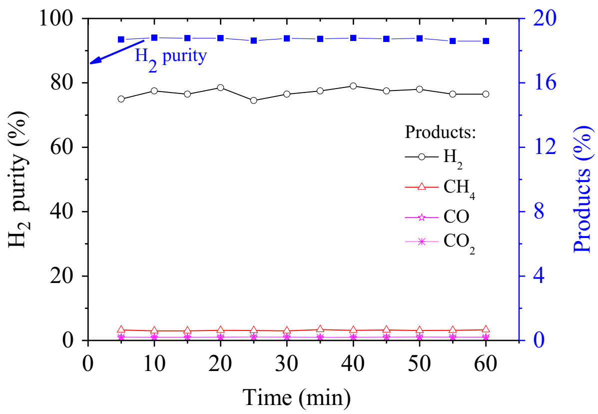


Fig. 7. Gas products with time by CSERP.

different reactors of a reformer and a regenerator, a riser, and two loop seals, and the results showed the conversion levels of methane are drastically lower in the fluidized bed reactor than that in the fixed-bed reactor, which indicates the necessity of using excess catalyst amount relative to a fixed bed situation. The analysis of the used sorbents indicates that only a fraction of the total CO_2 capacity was in use [73].

We recently developed direct high-purity H_2 generation from glycerol via the continuous sorption-enhanced steam reforming (CSERP) [74], and the process was characterized by a continuous flow concept of catalyst and sorbent for reaction and regeneration using two slow moving bed reactors. The integration of continuous steam reforming, WGS, CO_2 capture, and hydrogen separation in "one single reactor" can produce high-purity hydrogen, which can result in improved process efficiency and reduced capital costs. At the same time, the system produces a pure stream of CO_2 suitable for storage. The high-purity H_2 production is not needed to stop for generation both catalyst and sorbent. The schematic diagram of the system for continuous sorption-enhanced steam reforming of glycerol to high-purity hydrogen production was shown in Fig. 6. The proposed system of CSERP in Fig. 6 includes two moving-bed reactors by the integration of the hydrogen production with CO_2 capture in a typical reactor, and regeneration of catalyst and sorbent in other reactor. The riser was used for particles transport by N_2. The needle valves, seals and appropriate pressure balance prevented gas mixing between the reforming reactor and the regenerator. At the top of the reactor, the system for injecting the particles of catalyst and sorbent was used to compensate for loss during the runs. Fig. 7 depicts the gas products and H_2 purity for CSERP by a $Ni/NiAl_2O_4$ catalyst and a lime sorbent [74]. The high-purity H_2 is obtained at 550 °C during the operating time of 90 min and the decay in activity during the continuous reaction-regeneration of catalyst and sorbent is not observed. In fact, a number of parameters during the reaction and regeneration steps including the temperatures, residence times, and catalyst and sorbent properties play the significant roles in producing high-purity H_2. The studied showed that the first moving-bed reactor integrates well the continuous steam reforming, WGS and in-situ CO_2 removal while eliminating the need for a WGS catalyst under the conditions of 3.0 of S/C, the pressure of 1.0 atm, and the temperatures of 500 °C. The simultaneous regeneration of catalyst and sorbent can be well achieved by other moving-bed reactor. The calcination in the regenerator was employed with the mixture of steam and N_2, which lead to the regeneration of $CaCO_3$ formed and the gasification of coke deposited on the catalyst at the temperature of 900 °C. The effects of calcination conditions and methods on the capacities of sorbent and catalyst may be important, and sintering of catalyst should be avoided.

Table 2
Sorption capacities and regeneration temperatures for several sorbents [75–78].

Sorbent		Stoichiometric sorption capacity (mol/kg)	Regeneration temperature (°C)
Natural sorbents	Calcium carbonate, $CaCO_3$	17.96	900
	Dolomite, $CaCO_3 \cdot MgCO_3$	10.54	900
	Huntite, $CaCO_3 \cdot 3MgCO_3$	5.68	900
	Hydrotalcite, K-promoted hydrotalcite	0.65	400
Synthetic sorbents	Lithium orthosilicate, Li_4SiO_4	8.4	750
	Lithium zirconate, Li_2ZrO_3	6.5	690
	Sodium zirconate, Na_2ZrO_3	5.5	790

4.2. *How to select the sorbent?*

One should consider that the Ni catalyst also exposed to the CO_2 sorbent regenerating step could make its lifetime even shorter. Sorbent selection is very important and some products are showed in Table 2 together with sorption ability and regeneration temperature [75–78]. CaO has been reported to show strong affinity for CO_2 sorption and high sorption capacity of 17.8 CO_2 mol/kg at high temperature [75]. The effectiveness of both sorption-enhanced steam reforming and the use of Ca-based CO_2 sorbents have been demonstrated in previous works [66,67], and at the most favorable conditions, the total concentration of CO_2 in the product gas was low as 50 ppm [79–81]. Thermodynamic equilibrium for CO_2 capture using CaO showed that decreasing the temperature at a constant total pressure or increasing the total pressure at a constant temperature will promote capture of CO_2 by CaO sorbent [82,83]. In the SERP, the high-purity H_2 production has a very strong dependence on the in-situ CO_2 removal, and very fast sorption and regeneration rates of sorbent for CO_2 removal are required to allow for compact reforming and regeneration reactors. These properties for CaO sorbent are tested by continuous reaction with CO_2–N_2 mixture flow at 550 °C and high temperature regeneration with pure N_2 flow at 900 °C [83]. Fitting based on a model derived from the shrinking core models suggests that the reaction of CaO sorbent and CO_2 and H_2O is governed by a combination of the chemical reaction and product layer diffusion using the Unreaction Shrinking Core (USC) model [83]. Balasubramanian et al. showed that a gas with H_2 purity up to 95% was produced in a single reactor containing reforming catalyst and CaO sorbent [80]. For a typical CaO sorbent process, the typical operating temperatures are about 500–650 °C [83,84]. However, CaO material must be regenerated at high temperature of 900 °C and the cyclic stability of CaO in terms of CO_2 is significantly reduced due to the buildup of the irreversible $CaCO_3$ [85]. In same temperature conditions in the CSERP process, sintering of catalyst at high calcination temperatures causes decay in its activity.

Hydrotalcite is anionic clay consisting of positively charged layers of metal oxide or metal hydroxide with inter-layers of anions. Hydrotalcite materials have been found to have the CO_2 sorption capacity of 0.45–1.0 mol/kg at high temperature of 400–450 °C and steam has been determined to enhance its sorption capacity and stability [86–93]. Ding and Alpay studied CO_2 adsorption on hydrotalcites, and sorption saturation capacity of 0.58 mol/kg was measured in the presence of water vapor at 400 °C [89]. The reported rate of reaction for this kind of sorbents is too slow to compete with calcium-based ones, which may restrict its potential for an industrial scale [89,90]. Some studies also presented some experimental results on H_2 production through SE-SMR using the modified K_2CO_3-treated hydrotalcite materials as sorbents for CO_2 capture, and a large portion of CO_2 is easily recovered in the first few minutes of a desorption cycle and the complete recovery of CO_2 was achieved in a slower desorption

step [87,88,94]. The equilibrium data by the hydrotalcite materials for high temperature sorption of CO_2 obtained from a column apparatus can be adequately described by a Freundlich isotherm [89]. Oliveira et al. studied different hydrotalcite materials promoted with K or Cs in the temperature range of 400–510 °C and a bi-Langmuirian isotherm with physical adsorption and chemisorption is derived to describe the CO_2 sorption capacity over the different samples [92]. Hyun et al. carried out high-purity hydrogen production through sorption-enhanced WGSR using K_2CO_3-promoted hydrotalcite and the effects of various operating conditions of reaction on the process performance were studied [95]. The inconsistency observed in the illustration of the CO_2 sorption over hydrotalcite may principally be due to the large span of its composition, nature, preparation methods, promoter types and impregnation degree, reaction temperature and pressure range [87,96].

Lithium zirconate and lithium orthosilicate have received more attention due to their ability to retain good CO_2 chemisorption capacity at high temperature, and CO_2 sorption occurs in two steps: Li_2ZrO_3 decomposes according to the following reaction:

$$Li_2ZrO_3 \rightarrow 2Li^{+} + O^{2-} + ZrO_2 \quad (R5)$$

And the CO_2 gas dissolves as carbonate ions in Li_2CO_3 for the second step:

$$CO_2 + 2Li^{+} + O^{2-} \rightarrow Li_2CO_3 \quad (R6)$$

Nair et al. synthesized Li_2ZrO_3 using the sol–gel methods and studied its properties for high-temperature CO_2 separation, and results showed the material can store the significant quantities of CO_2 at high temperature and the reacted CO_2 can be regenerated by thermal cycling [97]. Ida and Lin studied the mechanism of the CO_2 sorption/desorption process on Li_2ZrO_3 by analyzing the phase and microstructure change of Li_2ZrO_3 [98]. It was shown that pure Li_2ZrO_3 absorbs CO_2 at high temperature with a slow sorption rate and addition of potassium carbonate and lithium carbonate to the Li_2ZrO_3 materials remarkably increases the CO_2 sorption rate [98,99]. Many studies have presented Li_2ZrO_3 sorbents for high temperature CO_2 capture properties [100–104]. We also studied the Lithium zirconate as one of the most promising materials for CO_2 sorption. Three Li_2ZrO_3 based sorbents with different Li/K were prepared by the solid-state method and the addition of lithium/potassium carbonate to Li_2ZrO_3 is proved to increase the CO_2 sorption rate compared to pure Li_2ZrO_3.

Although many metal oxides can react with CO_2 to form carbonates. However, not all metal oxides are suitable for CO_2 capture under conditions suitable for glycerol steam reforming. Metal oxides for steam reforming with in-situ CO_2 capture must satisfy several criteria [82,83]: (i) they should exhibit high reactivity in glycerol steam reforming at a temperature range of about 500–650 °C; (ii) the decomposition temperatures should be greater than steam reforming temperature; (iii) sorbent particles have good resistant to physical deterioration due to attrition or sintering; (iv) sorbent particles should be resistant to decay in reactivity through multiple CO_2 removal and release reactions; (v) rates of reaction and regeneration of sorbent should be high. Thus the advantage of a low cost sorbent is also very apparent. A number of synthetic oxides developed for high temperature CO_2 capture including Li_2ZrO_3 and Na_2ZrO_3 are likely to be prohibitively expensive. Abanades et al. argued that the performance of Li-based sorbents must be proven for up to ~10,000 reaction cycles to be economically competitive with sorbents derived from naturally occurring limestone [105].

4.3. *Sorption-enhanced chemical looping reforming process*

The chemical-looping reforming has been used for generation of H_2 and CO via cyclic reduction and oxidation of a solid oxygen carrier [106,107]. This overcomes the issue of coking of the catalyst. It also allows the steam reforming reaction to be performed at a lower temperature than the conventional steam reforming process by the close coupling of the endothermic reforming reaction with the exothermic Ni and C oxidation [108]. The fuel is fed to a separate reformer reactor, in which it is oxidized by oxygen provided via a solid oxygen carrier. The parts of the fuel may become completely oxidized to CO_2 and H_2O, but most of fuel should become partially oxidized to CO and H_2. A number of studies have also examined the chemical-looping reforming and the results indicated high reaction rate and good selectivity towards H_2 and CO for oxygen carriers including Ceria and Ni oxide catalysts for their redox properties [106–110]. Once NiO is reduced, some metallic Ni obtained has the excellent catalytic properties, facilitating steam reforming of hydrocarbon, water gas shift and a number of other reactions. A chemical-looping reforming process could be realized by circulating fluidized beds with oxygen carrier particles as bed material [110]. There has been suggested to combine chemical-looping reforming and sorption-enhanced reforming in one single process as the sorption-enhanced chemical looping reforming (SECLR), and the process for conversion of hydrocarbons to H_2 has been examined [106]. The process was conducted in three fluidized bed reactors. The reforming reactor was operated at low temperature and hydrocarbons were partially oxidized with oxygen provided by the oxygen carrier of NiO and with steam. Simultaneously, CO_2 produced is captured by the CO_2 sorbent. The overall reaction in the reforming reactor should be just about thermo neutral. CO_2 sorbent is regenerated in the calcination reactor producing a stream of pure CO_2. The air reactor was operated at high temperature and the oxygen carrier was reoxidized with air according to reaction. Unlike sorption-enhanced steam reforming, the SECLR process has potential to be self-sufficient with heat. This is because part of the oxidation is performed with O_2 provided via the solid oxygen carrier rather than with steam, and subsequent reoxidation of the oxygen carrier produce heat. If sufficient amount of this heat is transferred from the air reactor to the calcination reactor via the solids circulation, all three reactors could be operated without heating or cooling, which would be very elegant indeed. Pimenidou et al. studied high purity hydrogen production by SECLR process and the results has been shown to operate for 6 cycles at 600 °C at a steam to carbon ratio of 4 without obvious deterioration in fuel and steam conversion. 98% H_2 purity was obtained and long periods of autothermal operation within each cycle were demonstrated [111]. Lyon and Cole studied that H_2 rich syngas can be produced autothermally from methane and diesel fuel using a CLR system, also incorporating a calcium loop for CO_2-sorption enhancement of the steam reforming, and a crucial requirement of the process is that the fuel can reduce the solid oxygen carrier during the beginning of the fuel feed step to enable the steam reforming to start from cycle to cycle [112]. A lot of materials should be capable to convert fuel into H_2 at relevant conditions by SECLR process [113]. The chemical-looping reforming and SECLR processes are schematically showed in Fig. 8 [104,109]. The key issue in the system performance is the oxygen-carrier material and its stability. The oxygen-carrier material should accomplish some characteristics [104,111]: sufficient oxygen transport capacity; high reactivity for reduction and oxidation reactions; glycerol steam reforming and WGS reactions to H_2 production; resistance to attrition to minimize losses of elutriated solids; and environmental friendly and other some characteristics such as low cost. Chemical-Looping Combustion and Reforming technologies have been reviewed by Adanez et al. [113].

5. Conclusions

Thermal decomposition of glycerol plays a significant role in H_2 production from catalytic steam reforming. Many kinds of catalysts

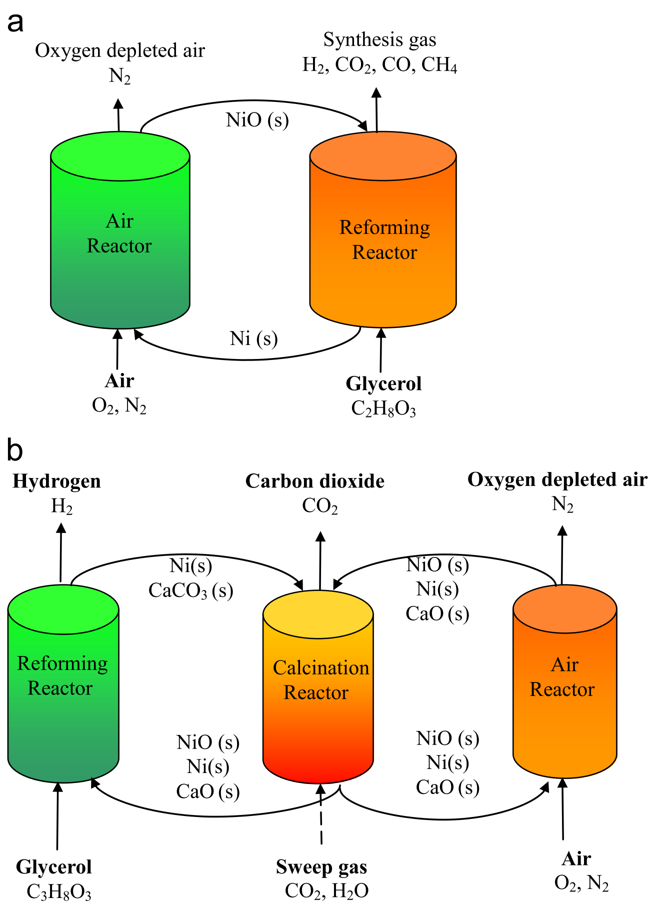


Fig. 8. Schematics of (a) chemical-looping reforming with NiO as oxygen carrier and (b) SECLR with NiO as oxygen carrier and CaO as sorbent.

have been investigated for glycerol steam reforming and some catalysts will undergo deactivation due to carbon formation. The conventional process of glycerol steam reforming is limited in H_2 productivity and the feedstock conversion due to the thermodynamic bounds of the reversible steam reforming reactions. The sorption-enhanced steam reforming process presents a potential intensified technique in which the co-generated CO_2 is selectively removed from the product gas mixture by an efficient sorbent. The process showed a high-purity H_2 production and high conversion of glycerol with very low impurities of CO, CH_4 and CO_2 at the temperatures (400–600 °C). For extended operation time, the continuous sorption-enhanced steam reforming of glycerol by a simultaneous flow concept of catalyst and sorbent for continuous reaction-regeneration using two slow moving bed reactors was proposed. The chemical-looping reforming and sorption-enhanced chemical looping reforming processes have potential to be self-sufficient with heat and the key issue in the system performance is the oxygen-carrier material and its stability.

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